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CHLORINE IN ILLINOIS COAL

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ABSTRACT

For the past 25 years or more, coals that have high alkali-chloride content have been recognized as likely to cause difficulties in high temperature steam boilers due to fouling and corrosion. The chlorine content of coal has been demonstrated to be an effective basis for estimating the degree of difficulty that may be expected.

Mapping of the percentage of chlorine in Herrin (No. 6) Coal in Illinois generally shows an increase in chlorine content toward the deeper parts of the Illinois Basin. The chlorine values range from zero near the outcrop of the coal, to values in excess of 0.60 percent in the deeper part of the basin.

Samples of both coal and ground water associated with the coal were taken from 13 mines. The chlorine content of the coal was found to be more closely related to the chlorine content of associated ground water than to depth. The general correlation of chlorine in coal with depth is the result of the increase in salinity of the ground water with depth.

Qualitative and semiquantitative tests demonstrating the evolution of chlorine have been made by heating chlorides at low temperatures in the presence of sulfur. Quantitative tests on total chlorine versus water soluble chlorine in coal and calculations of cation to anion mol ratios of both total and water soluble alkali chlorides have been made. No definite evidence of organically combined chlorine in Illinois coals has resulted from these investigations. It is the authors opinion that most, if not all, of the chlorine in Illinois coals occurs as inorganic chlorides, primarily sodium chloride. No Illinois coals are considered to be too high in chlorine for use as steam coals, although some may require special measures for their utilization.

INTRODUCTION

Interest in the mineral matter content of coal, and more specifically in the chlorine content, has shown a marked increase over the last 25 years. It was at the beginning of this period—coinciding with the start of World War II—that the power plants in Europe were called upon to produce at higher levels and for longer periods between shut-downs for servicing. Increased steam temperatures were demanded, and temperatures as high as 1050° F were obtained. Fireside temperatures on superheater tubes reached 1100° F and higher. A result of the increase in boiler output and temperature was an increase in the rate of fouling of the external heating surfaces of the boilers and in the amount of corrosion of boiler tubes.

The situation was especially acute in Great Britain. As a result, the Boiler Availability Committee was formed in 1941, arising out of the preexisting Deposits Committee. The Boiler Availability Committee was sponsored by the Central Electricity Generating Board, the South of Scotland Electricity Board, and the Water-Tube Boilermakers Association. The original aim of the committee was to conduct investigations into external deposits and corrosion, the results of which would enable the power stations of Great Britain to cope better with the enormous increase in demand. Boiler problems were aggravated, in many instances, by the adverse effect of changes in the fuel supplies that were brought about by the limitations on shipping of coal. The Boiler Availability Committee has been active continuously in the study of problems of boiler deposits and corrosion since its inception. The aspect of its research has changed from short term investigations, intended to enable the boiler plant load to be carried without regard to economic factors, to the current long term investigations into causes of various boiler troubles and their elimination. A large number of publications concerning research on boiler deposits and corrosion now exist. Most of these reports have originated in Great Britain and, specifically, from the Boiler Availability Committee.

The problems of boiler fouling and corrosion became of special interest in the United States following the initiation of the research in Great Britain. Reports relating to boiler deposits and corrosion appeared in this country in the middle 1940's, and the number of such reports increased during the following ten year period. Most of this research was carried on by the major boiler manufacturers.

Acknowledgments

The assistance of the coal operators in the collection of coal and water samples is greatly appreciated. Robert C. Baker assisted in the field by collecting many of these samples. The cooperation of the Illinois State Water Survey who did chemical analyses of more than 24 water samples and especially of Laurel M. Henley, Associate Chemist, is sincerely appreciated. All coal and ash analyses were made by the Analytical Chemistry Section of the Illinois State Geological Survey.

Boiler Deposits

Although the problems of fireside deposits and corrosion are closely associated, they will be separated somewhat in the short discussion to follow. Fireside deposits in steam generating boilers coat the heat-exchange tubes, thus reducing the rate of heat exchange. These deposits may partially or completely obstruct the

flow of gases through the various portions of the unit. Removal of these deposits often necessitates shutting down the boiler, which detracts from the economically important "boiler availability."

Deposits that build up on the radiant convection and superheater sections of a steam generating system generally are referred to as high-temperature deposits (Krause, 1959). These deposits have been classified by Crossley (1963) as:
(1) Phosphatic deposits. Phosphatic deposits are characterized chemically by from 10 to 35 percent phosphate (P_2O_5) in the inner layers. The deposits are the result of the production of pyrophosphoric acid ($H_4P_2O_7$) in the boiler. The pyrophosphoric acid condenses on the heat exchange surfaces and reacts to form hard crystalline phosphates (Crossley, 1952; Ely and Barnhart, 1963). The source of the phosphorous is probably the mineral fluorapatite ($Ca_5(PO_4)_3F$), which occurs in small amounts in most coals (Ely and Barnhart, 1963). Coals that caused difficulty due to the build up of phosphatic deposits contained from 0.04 to 0.08 percent phosphorous.
(2) Sintered and fused deposits. Sintered and fused deposits consist of fly ash particles that are bound together by partial or complete fusion. Chemically these deposits are similar in composition to coal ashes (Crossley, 1952).
(3) Alkali-bonded deposits. Alkali-bonded deposits constitute the most common cause of fouling of steam generation and superheater tubes. These deposits consist of fly ash, bonded in a matrix of sodium and potassium sulfates and pyrosulfates (Crossley, 1952, p. 224). The deposits often consist of a light colored inner layer that is very high in alkali sulfates and a darker outer layer that consists predominantly of fly ash. Deposits projecting into the hotter gases of the boiler may have distal portions that are predominantly alkali silicates (Anderson and Diehl, 1955).

A more complete discussion of the formation of fireside deposits in steam boilers can be found in the following reports: Crossley (1948; 1952; 1963); Carlile (1952); Crumley, Fletcher, and Wilson (1955); Michel and Wilcoxson (1955); Marskell and Miller (1956); Wickert (1958); Krause (1959); Grant and Weymouth (1962); and Ely and Barnhart (1963).

Corrosion

Although corrosion may affect many different portions of a steam boiler, corrosion of the superheater and reheater tube banks is the most detrimental type. This type of corrosion is increasing in importance. It is most prevalent where metal temperatures are between 1100° and 1300° F (Ely and Barnhart, 1963, p. 883). The wastage of these tube banks is always associated with deposits and occurs mainly on the side of the tube surface that faces into the gas stream (Samms and Smith, 1961, p. 457). Nelson and Cain (1960) observed that the deposits became molten between 1000° and 1300° F, and where molten in contact with the tube metal surface, the deposits react with the metal. The problems of superheater and reheater corrosion are expected to increase as higher steam temperatures are demanded. Recent review articles concerning corrosion in steam boilers have been written by Samms and Smith (1962), Slunder (1959), and Ely and Barnhart (1963).

Counteracting Boiler Fouling and Corrosion

A large amount of evidence, from both laboratory and field studies, indicates that a strong correlation exists between the severity of high temperature deposits and

corrosion and the composition of the coal. Coals that are high in alkalies, sulfur, and chlorine cause the most difficulties. Crossley (1963) presented a scheme whereby any British coal could be placed into one of four classes, based on chlorine percentage, ash percentage, and sulfur percentage.

A - free from corrosion
B - probably free from corrosion
C - possibly free from corrosion
D - risk of corrosion

Each of the four classes was then subdivided into, respectively, two, four, six, and eleven subclasses. In general, the higher the chlorine content, the greater is the possibility of corrosion. No coal containing over 0.40 percent chlorine was classified "A - free from corrosion." As the sulfur content increases, the risk of deposits and corrosion also increases. However, as the ash content increases, the possibility of problems with the coal decreases (Crossley, 1963). He suggested that this scheme could be used to give valuable information concerning individual coals, to rate coal blends, and to suggest the best combination of any two or more coals to be utilized in a single boiler plant.

In addition to the blending of coals to minimize deposit formation and associated corrosion, it may be possible to remove some of the deleterious constituents from the coal prior to firing. One instance of a marked decrease in total alkalies, following a two year period of storage, has been reported for a central Illinois coal (Michel and Wilcoxson, 1955). A current study of the weathering of a central Illinois coal over an 84 week period also shows this decrease in chlorine. The coal was crushed and sized to $\frac{1}{4}$ inch by 10 mesh and was left exposed out-of-doors with only a mesh screen over it to prevent contamination. The chlorine content decreased by one-half within an 8 week period and leveled off at approximately 36 percent of the original chlorine value after 24 weeks (John A. Harrison, personal communication). It is also possible to reduce the alkali chloride content of coal by washing. However, the amount that may be removed in this manner is probably small and may not be sufficient to alleviate specific problems. The amount that can be removed is dependent on the size consist of the coal being washed, composition of the wash water, original alkali chloride content of the coal, and duration of washing. Whether or not such a procedure is practical must be determined for each coal.

Other methods for preventing or minimizing these deposits are:

(1) Humidification of combustion air within the boiler has been suggested. Some minor success with the addition of steam to the combustion chamber has been reported, especially in cases of sintered and fused deposits (Gearing et al., 1955; Marskell and Miller, 1956; Freedman, 1956); however, the efficiency of steam in powder-fuel-fired boilers and in controlling alkali matrix deposits has been strongly questioned (Freedman, 1956).

(2) Some evidence of supression of the formation of the deposits by the introduction of solid additives such as kaolin and dolomite has been presented by Michel and Wilcoxson (1955).

(3) Proper operation and maintainence practices can be important factors in minimizing fouling and corrosion. Maintaining a proper balance of fuel and air input, the rate of mixing of fuel and air, and a proper cleaning schedule are examples of such practices (Ely and Barnhart, 1963).

(4) Equipment to be used in new boiler plants can be designed to best resist corrosion and fouling. This can be done by choosing alloys with the maximum resistance to corrosion in addition to the actual positioning of the various components.

These measures are most effective when the exact nature of the coal to be burned in the plant is known. Modifications also have been made on existing units to prolong the life of the most rapidly corroded tubes. For example, stainless steel sheets 1/8 inch thick, have been tack welded on the front of tubes in areas of marked corrosion (Jonakin, Rice, and Reese, 1959).

Although chlorine content that ranges from zero to 7.6 percent has been reported from deposits on superheater and reheater tubes (Carlile, 1952), chlorine content is generally low to absent in these deposits. Where reported, chlorine in deposits may be present in a smaller amount than is the chlorine in the coal. Therefore, there has been much discussion in the literature about the significance of chlorine in the formation of the deposits and in the corrosion of the tubes. It has been suggested that the percentage of the alkalies is the significant factor, and the chlorine content may be both incidental and innocuous. Although this controversy continues, the most widespread practice is to use the amount of chlorine in the coal as practical indication of the tendency for the coal to cause fouling and corrosion. When this practice is used, there is the added benefit that the data will not be confused by the inclusion of alkalies, which are combined in complex silicates and could be expected to remain in the ash (Crossley, 1963). It can be seen from figure 1 that this practice is applicable to Illinois coals. In general, the higher chlorine values and the higher total alkali values are found in the same coals. That the agreement between chlorine and alkali values is not better may be attributed to the problem of including in the analyses the Na and K combined in the clay minerals, in addition to the Na and K of the alkali halides.

Within Illinois, the interest in chlorine in coal has grown with the ever increasing amounts of Illinois coal being utilized in modern power plants operating at higher steam temperatures, with the concomitant possibility of complications arising therefrom (Michel and Wilcoxson, 1955; Anderson and Diehl, 1955; and Jonakin, Rice, and Reese, 1959). Within the last seven years, a large, relatively young mine in Illinois closed for the announced reason that coal from that mine caused "burning difficulties" when burned in high temperature units (Wall Street Journal, Midwest Edition, December 24, 1957). In addition to the interest in chlorine content of steam coals, there is also interest in the chlorine in coals used for making metallurgical coke. Chlorine appears in the tar produced in the coking process and may produce a corrosion problem, particularly in tar refining equipment.

No Illinois coals are considered to contain too high a chlorine content to be used in high temperature steam generating plants, although special precautions may be required in some instances. The following studies were undertaken to add to the general knowledge of the composition of Illinois coals and thereby allow informed decisions to be made concerning their utilization.

ANALYTICAL METHODS

The three analytical methods for determining chlorine in coal that have received the most attention are: the Eschka method, the bomb combustion method, and the high temperature combustion method. At the present time, the United States has no standard method for this determination, but the American Society for Testing and Materials Committee D-5 is currently working towards such a standard. This committee is giving most attention to the Eschka and bomb combustion methods. In addition, Technical Committee 27 of the International Organization for Standardization (ISO/TC 27) is proceeding

toward an international standard method or methods and is giving attention to all three methods mentioned above. Comparison of these methods, particularly by workers in England and in certain European countries, has indicated that results check closely.

In the Survey laboratory the Eschka method was used for some time. Occasional checks against the bomb combustion method indicated the results to be satisfactory. The Eschka method offers the advantage of analyzing several samples simultaneously. The reliability of this method is dependent on the low and uniform chlorine content of the reagent and possibly on another characteristic of the MgO, which will be discussed later.

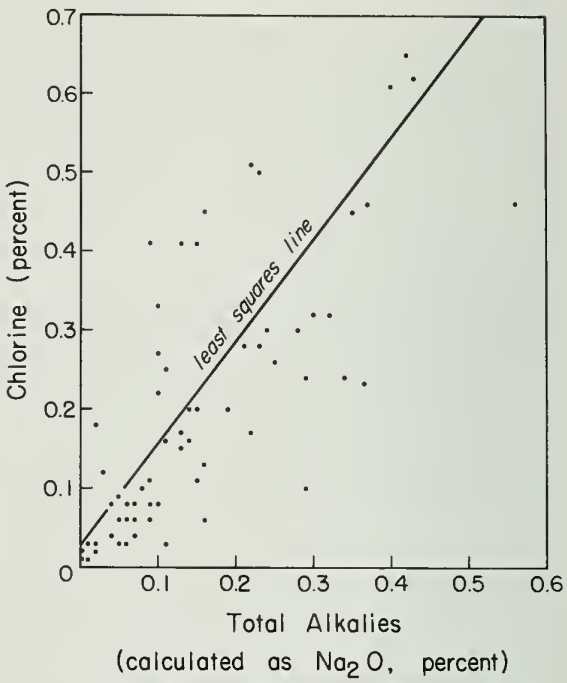

Figure 1 - Chlorine content plotted against total alkalies for Illinois coals.

On one occasion erratic chlorine values became evident and were traced to the Eschka mixture in use at the time. To eliminate this difficulty, an attempt was made to obtain reagent grade MgO and Na_2CO_3, but the only MgO that could be obtained locally was USP grade. The MgO and Na_2CO_3 were mixed (2 to 1 by weight). The mixture was found to be satisfactory in chlorine content, but when used for determining chlorine in coal, erratic results were obtained. According to American Chemical Society specifications for reagent grade MgO, loss on ignition should not exceed 2.0 percent. The loss on ignition of the USP grade MgO was found to be 10.5 percent. It appears that this characteristic may have been responsible for the unsatisfactory chlorine results. Reagent grade Mgo that met American Chemical Society specifications was obtained and using this in admixture with Na_2CO_3 gave satisfactory results in chlorine determinations. Due to the fact that Eschka mixture made from reagent grade chemicals is relatively expensive, the bomb combustion method, which requires only one fifth as much Eschka mixture, was used.

CHLORINE DISTRIBUTION IN ILLINOIS COALS

Sources of Data

During the 1930's, coals from a group of Illinois mines were sampled and chemically analyzed by State Geological Survey personnel. As part of the chemical analyses, a chlorine determination was made on each sample. Since 1948, it has been routine to make total and water soluble chlorine determinations on each suitable coal sample. In order to reduce the analytical error to a minimum and because of variations in analytical techniques, only data from the modern series of analyses (1948 to the present) were utilized directly in the preparation of the maps and graphs in this report. The samples were collected by Survey personnel

from freshly exposed areas within the mines and represent channels cut the full height of the coal seam. Chlorine values have also been determined on samples obtained from drill cores. However, these samples probably do not represent the total chlorine content of the coal seam. The values obtained may be as little as 60 percent of the true value in the coal or may approach the total true value. The discrepancy between chlorine determined on drill core samples and chlorine determined on face channel samples arises because some of the water soluble chlorine may be removed in solution by the water used in drilling the hole. Because of this discrepancy, only data for face channel samples are shown on the maps and graphs.

Chlorine Content of Herrin (No. 6) Coal

The Herrin (No. 6) Coal is mined extensively throughout much of the area of Pennsylvanian rocks in the Illinois Basin and therefore is well suited to a regional study of chlorine in coal. A chlorine isocon map, which will be referred to hereafter as an isochlor map, has been made for this coal seam (fig. 2). An isocon map is one on which lines of equal concentraion of some chemical parameter have been drawn, in this instance lines of equal chlorine content. Figure 2 was constructed using data from approximately 100 chemical analyses, representing 24 mines. The samples were obtained primarily from the southern, southwestern, and northwestern portion of the basin. The isochlores have been continued around the eastern half of the basin, where they are based on samples of No. 6 Coal from two mines and on interpretations made from oil field brines that were collected from Pennsylvanian strata. The data from the oil field brines were used because of the direct correlation between chlorine in groundwater and chlorine in coal, which will be demonstrated in subsequent paragraphs.

The chlorine content of the No. 6 Coal increases towards the center of the basin from the periphery. This general increase in chlorine content with depth can be observed by comparing the map showing depth to the coal (fig. 3) with the isochlor map (fig. 2). The agreement in configuration between the two maps is fairly good.

The relation between chlorine content of the coal and depth to the coal is shown graphically in figure 5. The agreement is fair, with a correlation coefficient of .86. Using the graph (fig. 5) and the isochlor map (fig. 2), it is possible to predict the coal chlorine values in any area that is underlain by the Herrin (No. 6) Coal. In most instances, such a prediction is reliable. However, in a few instances, such predictions have erred by nearly 100 percent toward both the higher and lower values. Such anomalous results are explained, at least generally, in subsequent discussion of the relation of the coal and the associated groundwater.

Chlorine Content of European Coals

Wandless (1957, p. 546) presented a map of the chlorine content of the coal seams in the East Pennine coalfield of the North Eastern and East Midlands Division of the central group of British coalfields. The chlorine content increases down dip from less than 0.15 percent to over 0.60 percent within a distance of 15 miles. Wandless (1957, p. 545) stated that the explanation of the phenomenon is likely to be complex and suggested some influence of vertical penetration and percolation by water through the overlying beds. Crumley and McCamley (1958, p. D-45) stated that in marine swamps the salinity of the soil would increase seaward, giving

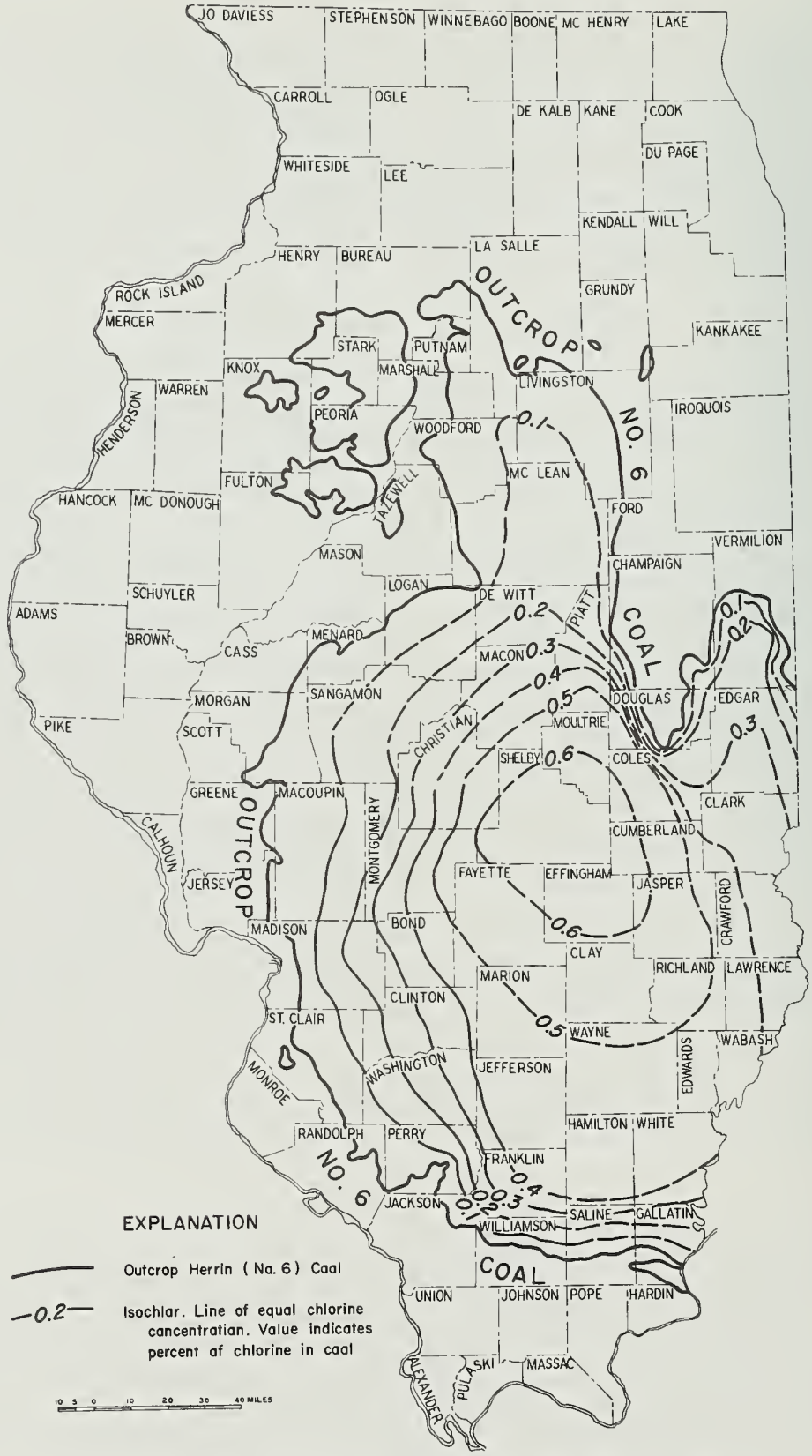

Figure 2 - Areal distribution of chlorine in Herrin (No. 6) Coal.

rise to euhalophytic vegetation (plants that must have saline water) near shore, miohalophytic vegetation (plants that can tolerate fairly high salinity) further inland, and the more normal glycophytic vegetation (plants that cannot tolerate high salinity) at the land edge of the swamp. The chlorine content of the vegetation also would increase seaward. They suggested that the control on the present chlorine distribution shown by Wandless (1957) in the East Midlands coalfields is the amount of chlorine that was absorbed by the coal-forming plants as inorganic chlorides.

An increase in chlorine and alkali content with depth also was reported for some of the German "Saltcoals" by Lehmann (1952). He demonstrated that the deeper portions of the synclinal coal basins contain the coals with the highest percentages of alkali halides. Lehmann attributed this increase with depth to the proximity to the underlying Permian (Zechstein) salt beds. He concluded that the salt that had been leached from the Zechstein beds was introduced into the coal by circulating ground water, with the highest concentrations developing in the coal beds nearest to the salt (Lehmann, 1952, p. 13).

It can be seen from the short preceding discussion that there are differences of opinion as to the origin of the chlorine in coal and also as to the explanation of the gradient from lower to higher chlorine values as the coals become deeper.

Chlorine Content in Ground Water

Within a single formation, the concentration of the various ions in ground water generally increases with depth (Bredehoeft et al., 1963, p. 257). Examples of this relation were given in isocon maps for the Ordovician of the Mid-Continent area by Case (1934, p. 857) and Dott and Ginter (1930, p. 1216). Plummer and Sargent (1931, plate 8) presented similar data from the Woodbine Sandstone (Cretaceous) of Texas. Meents et al. (1952) presented a series of 10 isocon maps of portions of the Illinois Basin, which included units from Ordovician through Mississippian age. These isocon maps (Meents, et al., 1952) show a general increase in the total dissolved solids with depth which closely outline the structure of the Illinois Basin.

Figure 4 is a plot of the brine concentration taken along an east-west line in the Illinois Basin. The curve was plotted from the isocon map of Devonian-Silurian brines given by Meents et al. (1952). The curve resembles a structure-section of the Devonian-Silurian units within the basin. The salinity profile, as drawn, corresponds closely to the structural profile, reflecting the deeper part of the basin, the LaSalle Anticline, and the Marshall-Sidell Syncline. The higher percentages of dissolved solids are found in the deeper areas, within the central part of the basin and in the syncline. The lower total dissolved solid values are in the shallower areas, on the crest of the anticline and the edges of the basin. The isocon maps mentioned above, with the exception of Plummer and Sargent (1931) who plotted chlorine content, have been constructed from values of total dissolved solids in the brines. However, inasmuch as they are brines, the chlorine content shows the same increase with depth as do the total dissolved solids. The chloride values for the brines in the Illinois Basin comprise approximately 60 percent of the total solids value in parts per million (Rees, and Tilbury, in Meents et al., 1952, p. 7).

Relation of Chlorine in Coal to Chlorine in Ground Water

Figures 2 and 3 show the increase of chlorine in the coal with depth in the Illinois Basin. The chlorine content of the ground water varies in a manner similar to the variation of the chlorine in the coal (fig. 4). In addition to the mines sampled only for chlorine in coal, 13 mines within Illinois and Indiana were sampled for chlorine in both coal and associated ground water. These mines were sampled in order to investigate a possible relation between the two similar trends. The 13 mines were distributed over a very wide area and ranged in depth from a little more than 100 feet to nearly 800 feet. Three face-channel samples of coal were taken at each mine and average values from analyses of the three samples were used in the interpretation of the data. Uncontaminated ground water samples also were collected at each mine. When possible three water samples were taken, either from the coal or the overlying shale. Samples were not taken from areas that had been rock dusted or where the water would come into contact with foreign materials (roof bolts, base plates, or timbers) before entering the collecting vessel. It was not possible to collect three water samples in all instances and a few mines are represented by a single water sample. Several mines within the basin that would be of interest in this study could not be sampled for water because of relatively dry conditions in the mines.

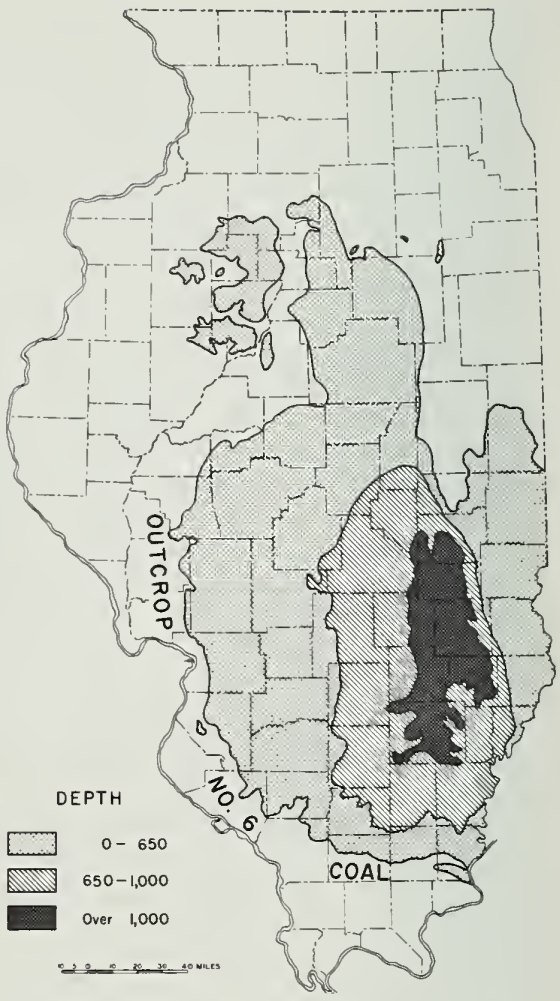

Figure 3 - Depth to Herrin (No. 6) Coal.

The relation of chlorine in coal to depth for these 13 mines is shown in figure 6. This chart is very similar to figure 5, except it is not restricted to Herrin (No. 6) Coal. Two of the samples are from other coal seams. The correlation coefficient of the data given in figure 6 is of the same magnitude as for figure 4 (.81 as compared to .86). Points labelled A and B represent average values for the two mines that are the furthest from the least squares line.

Figure 7 shows the relation between chlorine in the ground water and depth for the same 13 mines. The correlation coefficient is .79. This is again the same magnitude as obtained for chlorine in coal versus depth. Points A and B, representing values obtained from the same mines as in figure 6, lie the furthest from the "best fit" or least square line.

In both figures 6 and 7, point A lies to the low chlorine side of the line, and point B lies to the high chlorine side of the line. Relative to depth, mine A is "deficient" in chlorine in both the ground water and in the coal. Similarly, mine B has an "excess" of chlorine in both the coal and in the

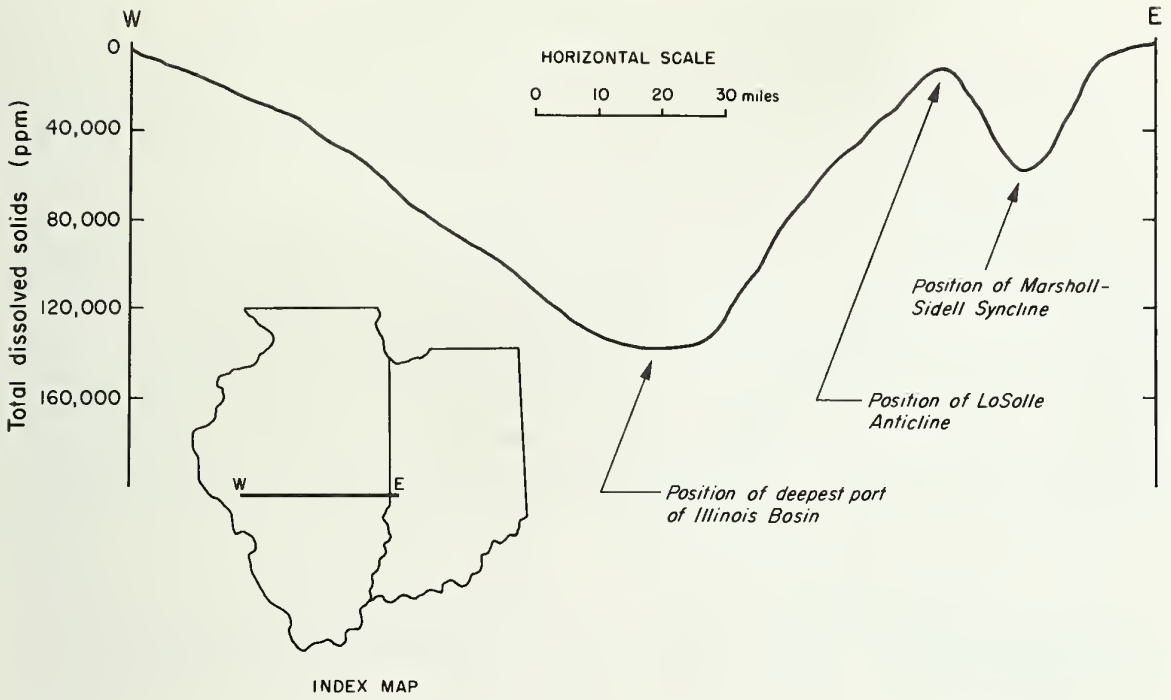

Figure 4 - Curve showing variations in total dissolved solids for Silurian-Devonian brines across the Illinois Basin. Data taken from isocon map presented by Meents, et al. (1952).

ground water relative to depth. The depth factor has been removed completely by plotting chlorine in coal versus chlorine in ground water for each mine (fig. 8). The correlation between the two variables is much better in figure 8 than for those in figures 6 and 7. The correlation coefficient is .93 as opposed to .81 and .79. Points A and B are now in much better agreement with the remainder of the data.

The primary control on the chlorine content of the coals sampled is apparently the composition of the ground water that is in contact with the coal. The fair-to-good correlation of chlorine in coal with depth is secondary, arising because of the general increase in salinity of the ground water with depth. This is shown by the coefficient of partial correlation. The coefficient of partial correlation is a relative measure of the association between two variables in a conditional distribution, for which one or more other variables are held fixed (Kendall and Buckland, 1957). In this case, the partial correlation coefficient for chlorine in coal relative to depth, eliminating the effect of chlorine in ground water, is 0.35 and for chlorine in coal relative to chlorine in ground water, irrespective of depth, is 0.81. This latter value (0.81) is extremely significant statistically (within 1 percent confidence limits); whereas the former value (0.35) has practically no significance. Anomalous values for the chlorine content of the ground water, values that are either unusually high or unusually low relative to the depth of the sample (points A and B on figure 7), must be interpreted individually, based on possible mechanisms for the concentration of brines, movements of the water in the basin, and the local geologic features, such as faulting, that might effect the hydrologic conditions. A basis on which such interpretations might be made was given by Bredehoeft et al. (1963), who discussed the concentration of brines and the movement of ground water in the Illinois Basin.

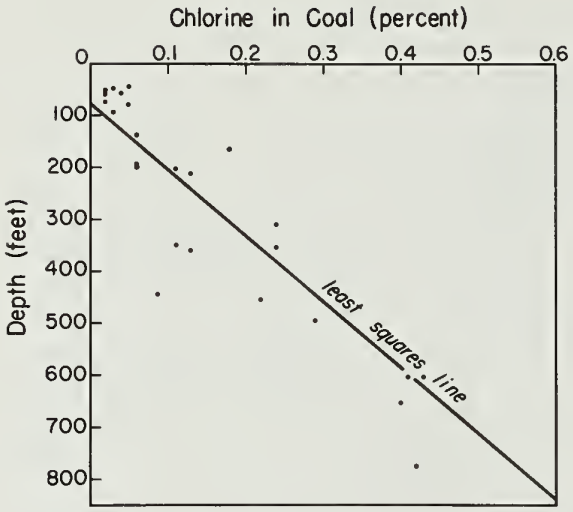

Figure 5 - Chlorine content of No. 6 Coal plotted against depth. Data for 26 mines in Illinois Basin.

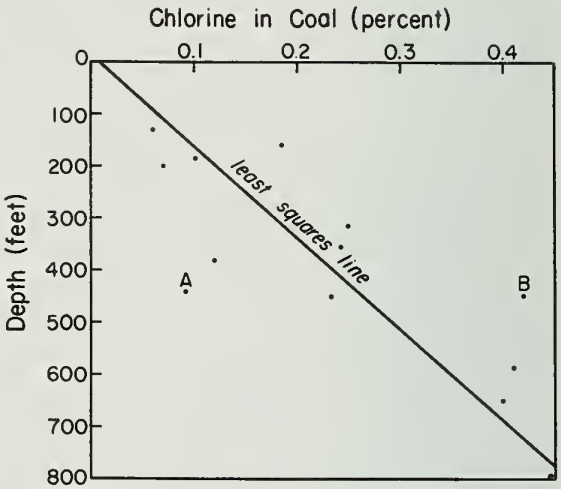

Figure 6 - Chlorine content of coal plotted against depth. Data for 13 mines sampled for both ground water and coal.

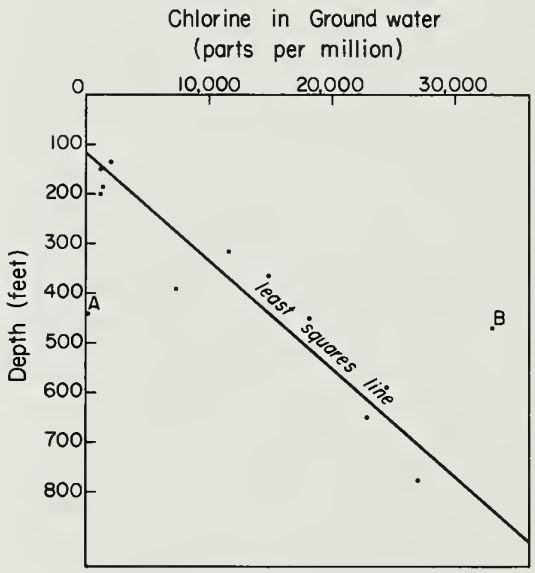

Figure 7 - Chlorine content of ground water plotted against depth. Data for 13 mines sampled for both ground water and coal.

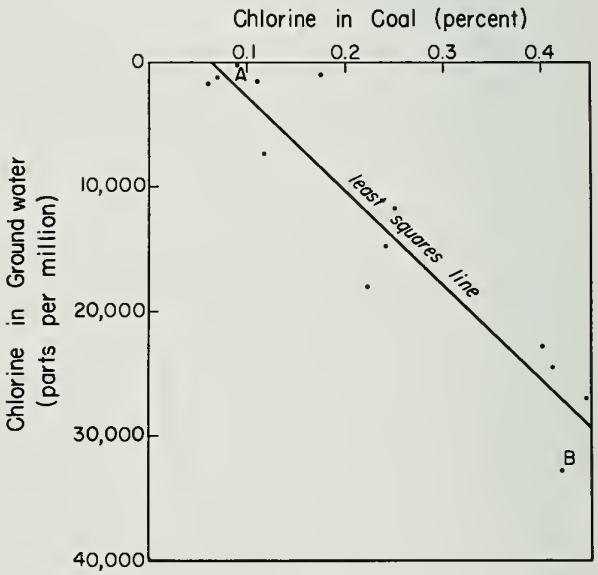

Figure 8 - Chlorine content of coal plotted against chlorine content of ground water. Data for 13 mines sampled for both ground water and coal.

MODE OF OCCURRENCE OF CHLORINE IN ILLINOIS COALS

The mode of occurrence of chlorine in coal has received some attention by European investigators, but the authors are not aware of much published work of this kind regarding United States coals, particularly Illinois coals.

There are two schools of thought on the manner of occurrence of chlorine in coal. The first is that chlorine occurs in coal almost entirely as inorganic chlorides. The chlorides most commonly thought to be present are sodium, potassium, and calcium chlorides, and in some instances magnesium and iron chlorides (DeWaele, 1915; Sexton and Davidson, 1921; Crossley, 1952; Whittingham, 1954).

The other school of thought is that the chlorine occurs partially in combination with organic matter (Brame and King, 1935; Edgcombe, 1956; Daybell and Pringle, 1958).

Because of the experimental results the authors are of the opinion that most, if not all, of the chlorine occurs as inorganic chlorides. Further discussion of this will be presented following the description and results of our experimental work.

Volitilization of Chlorine in Coal at Low Temperatures

In considering how chlorine might occur in coal, it has been suggested that part occurred in inorganic combination (chlorides) and part in organic combination. This conclusion has been stated most recently by British workers studying coals from the Midlands coalfield. Edgecombe (1956) concluded that more than half of the chlorine is held on the organic fraction as chloride ions because of the imbalance between water soluble alkali and water soluble chlorine, and also because chlorine can usually be driven off by heating the coal in air at 200° C. Daybell and Pringle (1958) concur with Edgecombe (1956) and state that the chloride ion is attached to the coal substance by a linkage with ion exchange properties. If no chlorine was lost during ashing at a temperature below the vaporization and decomposition temperatures of the inorganic chlorides, it might indicate that all the chlorine was in inorganic combination.

In order to investigate evolution of chlorine at low temperatures, a sample of coal that contained 0.36 percent total chlorine was ashed. The chlorides, which were considered most likely to be present, were sodium and potassium chlorides and possibly calcium and magnesium chlorides. From decomposition temperature and vapor pressure data for these chlorides, it was determined that it was safe to ash at a temperature not to exceed 500° C. Total chlorine was determined on the ash, calculated to the original coal basis, and found to be 0.13 percent. This experiment indicated the loss of about 64 percent of the chlorine during ashing at this comparatively low temperature. At first these results might be interpreted as evidence of organically combined chlorine in the coal. However, even though loss of inorganic chlorine by decomposition or volatilization of chlorides was not probable, it is possible that there was an interaction with other constituents of the coal to cause loss of chlorine. To study this possibility certain qualitative tests were made.

Various mixtures were heated in a pyrex tube at a temperature not exceeding 500° C. The tube was provided with an inlet and outlet to permit passing air through it during heating and passing the gaseous products through silver nitrate (acidified with HNO_3) to detect any evolution of chlorine. The results of these tests are shown

below. In the column headed "Chlorine Indication", the sign + represents indication of chlorine evolution, ++ indication of greater chlorine evolution, and - no chlorine evolution.

Mixtures	Chlorine Indication
Coal with the air undried but not wet	+
NaCl with the air undried but not wet	-
Coal + NaCl with the air undried but not wet	++
NaCl + lampblack, with the air undried but not wet	-
Clay (40% Al_2O_3), with the air undried but not wet	-
Clay + NaCl, with the air undried but not wet	-
Clay + NaCl + lampblack, with the air undried but not wet	-
NaCl + FeS_2, with the air undried but not wet	++
NaCl + FeS_2, with the air dried	++

As indicated above, heating NaCl alone did not result in evolution of chlorine. However the tests did show that chlorine is evolved presumably through interaction with other materials. Chlorine was evolved only in those cases where sulfur was present. When NaCl was heated with FeS_2, strong evolution of chlorine resulted, regardless of whether circulating air was moist or dry. Simple heating of coal containing 1.1 percent total sulfur (both pyritic and organic) caused some evolution of chlorine. When this same coal was heated with additional NaCl, a greater amount of chlorine evolved. Apparently, carbon (lampback) and clay do not react with NaCl to liberate chlorine.

From the above experiments, it must be concluded that chlorine in inorganic combination may be evolved from coal, probably through interaction with sulfur containing compounds, even during low temperature ashing. A logical explanation of this might be that sulfur is converted to SO_2 or SO_3, and this SO_2 or SO_3 may react with inorganic chlorides to liberate chlorine. Hence, we have no definite evidence, at this point, of the presence of organically combined chlorine.

Water Soluble Chlorine vs Total Chlorine

Another approach to the question of the mode of occurrence of chlorine in coal was based on the thought that inorganically combined chlorine (chlorides) should be water soluble while organically combined chlorine might not be appreciably soluble in water. We have analyzed many of the coal samples for both total and water soluble chlorine. The method used for determining the water soluble chlorine was empirical and consisted of extracting a weighed sample of minus 60 M coal with water at 80° C for one hour. The coal was then filtered off, and chlorine in the filtrate was determined by titration.

Chlorine values, both total and water soluble, for face channel samples are shown in table 1. The data have been arranged according to counties, and while some chlorine values for coals from several counties appear in the table, only those for Christian, Franklin, Jefferson, and Williamson Counties are considered here. Chlorine values for coals from other counties are so low, for the most part, that little chlorine trouble could be expected from normal use of the coals. Actually the amount of chlorine in these coals are often so near the tolerance of the analytical methods used that they are of doubtful significance so far as this study is concerned.

A large amount of total chlorine of the Christian County coals was extracted in water (an average of 81 percent). Definitely lower percentages of the total chlorine

of Franklin and Williamson County coals were extracted with water (averages of 31 and 23 percent respectively). The percentage of water extractable chlorine in the Jefferson County coals was intermediate (an average of 61 percent).

The wide variance in the percent of the total chlorine extractable in water could be interpreted as evidence of the presence of organically combined chlorine in greater proportion for those coals that showed lower water soluble chlorine. However there is another, and possibly more plausible, explanation for this. In order to accomplish extraction it is necessary for the water to come into contact with the inorganic chlorides. From knowledge of the ultra-fine structure of coal, it seems reasonable to assume that these chlorides are in the coal capillaries. These capillaries must be broken down in order to achieve extraction of the chlorides. Therefore, the finer the coal is ground, the more inorganic chlorine could be extracted with water. This is the case as has been demonstrated by the authors and other investigators.

In the laboratory, a coal containing 0.42 percent total chlorine gave 0.12 percent water soluble chlorine on the minus 60 mesh (250 micron) size. The same coal ground to 89 percent minus 5 micron size showed 0.29 percent water soluble chlorine. While the amount of chlorine extracted from the very finely ground coal was more than twice that extracted from the 60 mesh coal, it will be noted that only 69 percent of the total chlorine was recovered by water extraction, even though very fine grinding was accomplished. This should not be too surprising, however, when one considers that coal pore size distribution calculations by Machin et al. (1963) showed a high peak in the region of 40 angstroms diameter and that 5 microns are equal to 50,000 angstrom units. It would appear difficult to grind coal fine enough to achieve complete water extraction of all inorganic chlorine in coal. It is interesting to note, however, that Edgcombe (1956) reported almost complete water extraction of chlorine from the British coals with which he worked. Also as discussed previously, the Christian County coals yeilded, on the average, over 80 percent water soluble chlorine by the method described in this report.

In another experiment, a 5 gram sample of minus 60 mesh coal that contained 0.45 percent total chlorine was leached with water at room temperature. The sample was stirred periodically, and at the end of various extraction times, the solutions were filtered from the coal and fresh water added. Extraction time for each portion of fresh water was 1, 20, 20, 25, 25, and 72 hours or a total extraction time of 163 hours. In general, progressively lesser amounts of chlorine were extracted with each increment of water added, but a measurable amount of chlorine was extracted in the last increment of water. The total chlorine found in the residual coal was 0.19 percent. Thus only 58 percent of the chlorine originally present in this coal was extracted, even with 163 hours (almost 7 days) extraction time. Just how long it might take to accomplish complete water extraction of soluble chlorine from this coal, or whether it would be possible at all, is not known, but these data indicate that such extraction is a slow process. These observations would seem to agree with the idea that the chlorine may be in the fine capillaries of the coal, thus preventing ready extraction.

Another approach to the question of how chlorine occurs in coal has been to consider the ratio of cations to the anion chlorine. If there is a significant deficiency of cation for combination with chlorine as chloride, it might indicate that part of the chlorine was present in organic combination. Both total and water soluble sodium (Na) and potassium (K) determinations were made. To date, other cations that might be present as chlorides have not been analytically determined.

TABLE 1 – TOTAL AND WATER SOLUBLE CHLORINE OF ILLINOIS COALS
(all face channel samples)

Lab No.	County	Coal No.	Total Chlorine % (Dry)	Water Soluble Chlorine % (Dry)
C–10965	Adams	2	.04	.00
C–11009	Adams	2	.03	.02
C–11010	Adams	2	.02	.02
C–10963	Brown	2	.04	.01
C–10964	Brown	2	.05	.02
C–12510	Bureau	6	.02	.02
C–12511	Bureau	6	.02	.01
C–12512	Bureau	6	.02	.02
C–10291	Christian	6	.22	.19
C–10292	Christian	6	.24	.23
C–10293	Christian	6	.26	.20
C–10142	Christian	6	.62	.50
C–10143	Christian	6	.65	.48
C–10144	Christian	6	.61	.45
C–13056	Douglas	6	.07	.03
C–13057	Douglas	6	.07	.02
C–13058	Douglas	6	.07	.02
C–10603	Franklin	6	.22	.02
C–10604	Franklin	6	.25	.06
C–10605	Franklin	6	.27	.07
C–11621	Franklin	6	.41	.02
C–11622	Franklin	6	.41	.02
C–11744	Franklin	5	.20	.03
C–11745	Franklin	5	.20	.03
C–12828	Franklin	6	.21	.09
C–12829	Franklin	6	.23	.11
C–12832	Franklin	6	.21	.12
C–12833	Franklin	6	.26	.11
C–12834	Franklin	6	.26	.09
C–13215	Franklin	6	.40	.19
C–13216	Franklin	6	.39	.13
C–13217	Franklin	6	.41	.14
C–12630	Fulton	2	.00	.00
C–12631	Fulton	2	.00	.00
C–12423	Fulton	5	.01	.00
C–12424	Fulton	5	.01	.00
C–12425	Fulton	5	.01	.01
C–12426	Fulton	5	.01	.01
C–11011	Fulton	2	.04	.01
C–10288	Jefferson	6	.51	.28
C–10289	Jefferson	6	.45	.19
C–10290	Jefferson	6	.50	.36
C–10582	Jefferson	6	.36	.23
C–10583	Jefferson	6	.27	.16
C–10584	Jefferson	6	.27	.12
C–10616	Jefferson	6	.38	.29
C–10668	Jefferson	6	.33	.26
C–10614	Kankakee	2	.04	.04
C–10615	Kankakee	2	.04	.04
C–11223	Kankakee	"Cardiff"	.06	.01
C–11224	Kankakee	5	.14	.01
C–11225	Kankakee	5	.12	.01
C–11222	Kankakee	2	.02	.02
C–12506	Knox	6	.03	.02
C–12508	Knox	6	.02	.02
C–12507	Knox	6	.02	.01
C–11051	Macoupin	6	.13	.04
C–11052	Macoupin	6	.11	.04
C–11053	Macoupin	6	.09	.04
C–13066	Macoupin	6	.09	.06
C–13067	Macoupin	6	.08	.08
C–13068	Macoupin	6	.08	.06
C–13065	Macoupin	6	.07	.03
C–11313	Madison	6	.06	.01
C–10799	Madison	6	.12	.10
C–10807	Madison	6	.13	.09
C–11686	Madison	6	.06	.02
C–11091	Madison	6	.07	.03
C–11092	Madison	6	.00	.00
C–12537	Marion	6	.47	.32
C–12538	Marion	6	.44	.33
C–12539	Marion	6	.38	.21
C–10482	Mercer	6	.06	.04
C–12442	Montgomery	6	.11	.09
C–12443	Montgomery	6	.10	.04
C–12444	Montgomery	6	.12	.07
C–12445	Montgomery	6	.17	.13
C–12420	Peoria	2	.04	.01
C–12421	Peoria	2	.04	.00
C–12640	Perry	6	.03	.03
C–12641	Perry	6	.03	.03
C–12642	Perry	6	.05	.04
C–13070	Randolph	6	.07	.04
C–13071	Randolph	6	.03	.04
C–13072	Randolph	6	.05	.04
C–12472	St. Clair	6	.02	.02
C–12473	St.Clair	6	.02	.01
C–12474	St.Clair	6	.03	.02
C–12476	St. Clair	6	.05	.02
C–12477	St. Clair	6	.05	.04
C–12478	St. Clair	6	.05	.05
C–12969	Saline	4	.16	.02
C–12970	Saline	4	.22	.01
C–12971	Saline	4	.13	.04
C–10617	Saline	5	.06	.05
C–11200	Saline	Davis	.12	.01
C–11201	Saline	Davis	.16	.01
C–11202	Saline	Davis	.08	.01
C–12492	Sangamon	5	.19	.16
C–12493	Sangamon	5	.18	.15
C–12494	Sangamon	5	.17	.13
C–12496	Schuyler	5	.03	.01
C–12497	Schuyler	5	.05	.02
C–12498	Schuyler	5	.04	.04
C–12502	Stark	6	.04	.04
C–12503	Stark	6	.03	.02
C–12504	Stark	6	.03	.02
C–12570	Vermilion	7	.03	.02
C–13198	Vermilion	6	.22	.16
C–13199	Vermilion	6	.23	.18
C–13200	Vermilion	6	.21	.15
C–11496	Vermilion	7	.12	.03
C–11497	Vermilion	7	.15	.03
C–11498	Vermilion	7	.08	.03
C–11499	Vermilion	7	.13	.03
C–12520	Vermilion	7	.16	.10
C–12458	Williamson	6	.28	.10
C–12459	Williamson	6	.25	.09
C–12460	Williamson	6	.25	.08
C–12939	Williamson	6	.16	.03
C–12940	Williamson	6	.19	.03
C–12941	Williamson	6	.16	.03
C–12943	Williamson	6	.07	.03
C–12944	Williamson	6	.06	.01
C–12945	Williamson	6	.15	.01
C–12462	Williamson	5	.08	.02
C–12463	Williamson	5	.08	.01
C–12454	Williamson	6	.06	.00
C–12455	Williamson	6	.05	.00
C–12456	Williamson	6	.03	.00
C–11213	Williamson	6	.06	.01
C–11214	Williamson	6	.06	.01
C–11215	Williamson	6	.10	.01
C–12785	Williamson	6	.16	.03
C–12786	Williamson	6	.18	.05

Values expressed as mol percent for total chlorine, sodium, and potassium and mol ratios of Na + K to Cl are presented in table 2. Similar data are also shown graphically in figure 1, where total alkalies as Na_2O, are plotted against total chlorine. Similar water soluble data are presented in table 4. Most of the data are from Christian, Franklin, and Jefferson County coals.

If all the chlorine in coal were present as the chlorides of sodium and potassium, the mol ratio of Na + K to Cl would be one. All the samples that were analyzed from Christian County showed a ratio of Na + K to Cl greater than one, the average for all samples being 1.5268 (table 2). Thus, there was more than enough Na + K to account for all the chlorine. The excess of Na and K probably was present in the silicates of the mineral matter. In fact, the presence of excess Na + K does not exclude the possibility of the presence of chlorides other than those of sodium and potassium, as the data in table 3 indicate. This will be discussed later.

Some of the samples from Franklin County showed an excess of Na + K over Cl; others showed a deficiency (table 2). The average mol ratio for all coals analyzed was 0.9302, indicating an overall deficiency of Na + K. This might be interpreted as an indication of the presence of a small amount of organically combined chlorine, but a more logical interpretation is that it is an indication of the presence of other undetermined cations. For the Jefferson County coals, the average mol ratio of 0.7866 indicates a distinct deficiency of Na + K. The explanation offered above for the Franklin County coals might apply.

Values expressed as mol percent for water soluble chlorine, sodium, and potassium and the mol ratios of Na + K to Cl are presented in table 3.

For the Christian County coals, the average mol ratio was 0.8541, indicating a deficiency of water soluble Na + K for the water soluble Cl present. Earlier, attention was called to the fact (table 2) that an excess of total Na + K over Cl might not exclude the possibility of the presence of chlorides other than those of sodium and potassium. The fact that there was less than enough Na + K for the Cl in the water extracts would seem to emphasize this possibility.

For the Franklin County coals, the average ratio was 1.1476, indicating more than enough Na + K for the Cl in the water extracts. For the Jefferson County coals, the average ratio was 0.5954, indicating a deficiency of Na + K for the Cl. However, in this instance, data are too few to allow firm conclusions to be drawn.

Because no difinite evidence of organically combined chlorine in Illinois coals has resulted from these studies and because organic-chlorine compounds are rare in natural materials such as plants, the authors are of the opinion that most, if not all, of the chlorine in Illinois coals occurs as inorganic chlorides.

PROBLEMS ASSOCIATED WITH CHLORINE IN COAL PREPARATION

Reducing the chlorine content of coal by washing has been suggested as a possible remedy for the problem of high chlorine coals. As indicated in previous paragraphs, however, many coals appear to have only a small percentage of chlorine that can be readily extracted by water.

In one series of tests, most of the wash water in a preparation plant was replaced with "fresh" water. Subsequently, samples of both coal and wash water were taken at the beginning and end of each shift for nearly two weeks. The dissolved solids in the wash water were 0.03 percent by weight at the beginning of the

TABLE 2 — TOTAL CHLORINE, SODIUM, AND POTASSIUM EQUIVALENT PERCENT

County	Lab. No.	Chlorine	Na	K		Ratio $\frac{Na+K}{Cl}$
Christian	C-10142	0.0175	0.0155	0.0030		1.0571
Christian	C-10143	0.0183	0.0152	0.0036		1.0273
Christian	C-10144	0.0172	0.0148	0.0032		1.0465
Christian	C-10160	0.0130	0.0155	0.0042		1.5154
Christian	C-10161	0.0130	0.0136	0.0042		1.3692
Christian	C-10162	0.0090	0.0110	0.0045		1.7222
Christian	C-10163	0.0085	0.0100	0.0040		1.6471
Christian	C-10237	0.0051	0.0058	0.0038		1.8824
Christian	C-10242	0.0175	0.0145	0.0034		1.0229
Christian	C-10243	0.0169	0.0139	0.0034		1.0237
Christian	C-10244	0.0166	0.0134	0.0036		1.0241
Christian	C-10245	0.0164	0.0145	0.0057		1.2317
Christian	C-10246	0.0189	0.0171	0.0072		1.2857
Christian	C-10254	0.0079	0.0068	0.0045		1.4304
Christian	C-10291	0.0062	0.0071	0.0045		1.8710
Christian	C-10292	0.0068	0.0158	0.0055		3.1324
Christian	C-10293	0.0073	0.0106	0.0053		2.1781
Christian	C-10294	0.0068	0.0084	0.0053		2.0147
					Average	1.5268
Franklin	C-10603	0.0062	0.0042	0.0034		1.2403
Franklin	C-10604	0.0071	0.0048	0.0032		1.1268
Franklin	C-10605	0.0076	0.0042	0.0030		0.9474
Franklin	C-10634	0.0082	0.0039	0.0070		1.4878
Franklin	C-10635	0.0087	0.0039	0.0047		0.9885
Franklin	C-10636	0.0093	0.0039	0.0038		0.8280
Franklin	C-10637	0.0096	0.0029	0.0036		0.6771
Franklin	C-10638	0.0082	0.0032	0.0038		0.8537
Franklin	C-10639	0.0113	0.0068	0.0057		1.1062
Franklin	C-10640	0.0082	0.0035	0.0068		1.2561
Franklin	C-10641	0.0087	0.0029	0.0025		0.6207
Franklin	C-10642	0.0090	0.0035	0.0040		0.8333
Franklin	C-10643	0.0099	0.0039	0.0051		0.9091
Franklin	C-10836	0.0116	0.0048	0.0032		0.6897
Franklin	C-10837	0.0087	0.0039	0.0032		0.8161
Franklin	C-10945	0.0093	0.0032	0.0038		0.7527
Franklin	C-10946	0.0107	0.0055	0.0085		1.3084
Franklin	C-11621	0.0116	0.0042	0.0036		0.6724
Franklin	C-11622	0.0116	0.0029	0.0036		0.5603
					Average	0.9302
Jefferson	C-10288	0.0144	0.0071	0.0045		0.8056
Jefferson	C-10289	0.0127	0.0035	0.0034		0.5433
Jefferson	C-10290	0.0141	0.0074	0.0036		0.7801
Jefferson	C-10463	0.0102	0.0174	None		1.7059
Jefferson	C-10463	0.0082	0.0058	None		0.7073
Jefferson	C-10464	0.0039	0.0032	None		0.8205
Jefferson	C-10465	0.0031	0.0035	None		1.1290
Jefferson	C-10616	0.0107	0.0039	None		0.3645
Jefferson	C-10618	0.0130	0.0029	None		0.2231
					Average	0.7866

TABLE 3 — WATER SOLUBLE CHLORINE, SODIUM, AND POTASSIUM EQUIVALENT PERCENT

County	Lab. No.	Chlorine	Na	K		Ratio $\frac{Na+K}{Cl}$
Christian	C-10142	0.0141	0.0123	None*		0.8723
Christian	C-10143	0.0135	0.0113	None*		0.8370
Christian	C-10144	0.0127	0.0116	None*		0.9134
Christian	C-10242	0.0141	0.0113	None*		0.8014
Christian	C-10243	0.0149	0.0106	None*		0.7114
Christian	C-10244	0.0152	0.0110	None*		0.7237
Christian	C-10245	0.0158	0.0110	None*		0.6962
Christian	C-10246	0.0169	0.0139	None*		0.8225
Christian	C-10293	0.0056	0.0061	None*		1.0893
Christian	C-10294	0.0054	0.0058	None*		1.0741
					Average	0.8541
Franklin	C-10603	None*	0.0019	None*		- - -
Franklin	C-10604	0.0017	0.0023	None*		1.3529
Franklin	C-10605	0.0020	0.0019	None*		0.9500
Franklin	C-10836	0.0031	0.0023	None*		0.7419
Franklin	C-10837	0.0020	0.0016	None*		0.8000
Franklin	C-10945	0.0011	0.023	None*		2.0909
Franklin	C-10946	0.0020	0.0019	None*		0.9500
					Average	1.1476
Jefferson	C-10288	0.0079	0.0045	None*		0.5696
Jefferson	C-10289	0.0054	0.0035	None*		0.6481
Jefferson	C-10290	0.0102	0.0058	None*		0.5686
					Average	0.5954

* Less than 0.0004

period, rose to 0.23 percent within less than 48 hours. Then the wash water composition remained relatively constant for the remainder of the test period and was in apparent equilibrium with the coal. The chlorine content of the clean coal was essentially the same as the raw coal entering the plant.

The findings on the water soluble chlorine of coal reported previously would seem to indicate that effectiveness of removal of chlorine by water washing will vary for different coals. The significance of analytical values for water soluble chlorine as obtained by the Illinois Geological Survey laboratories is limited. They should be considered relative rather than absolute values. However, they may have qualitative use in indicating the effectiveness of water washing in reducing the chlorine content of certain coals.

A liberal fresh water flushing of the coal will, in most cases, reduce the quantity of chlorine in a washed coal sample; however, the amount by which it is reduced may be relatively small. Each case would have to be studied to determine if there was a significant reduction. Such steps might be effective in only those instances where the fresh water is actually low in total dissolved solids. Water that is continually recycled from a settling pond may have a relatively high dissolved salt content after a period of only a few years.

In several instances, a white stain that was observed on oil treated stoker coals was found to be related to dissolved salts in the wash water. Although in

these cases the amount of deposit was so small that the quality of the coal was unaffected, some consumer objections were encountered. It is possible that this problem may be eliminated by an adequate fresh water rinse at the end of the washing operations.

Limited data suggest that coals that have marginal chlorine content may change to problem coals because of the addition of calcium or sodium chloride solution to prevent freezing during transportation.

SUMMARY AND CONCLUSION

Data from the investigations reported here have indicated that the mode of occurrence of alkali chlorides in the coals studied does not differ fundamentally from the occurrence in the coals, particularly from Great Britain, which have been extensively reported in the literature. However, conclusions based on these data do not, in all cases, agree with those in the literature.

It has been possible to plot the areal distribution of chlorine in Herrin (No. 6) Coal in the Illinois Basin and by connecting points of equal chlorine content to construct a meaningful isochlor map. Although the isochlor map was constructed primarily on the basis of chemical analyses of face channel samples of coal, data from analyses of water samples taken near the stratigraphic horizon of No. 6 Coal also were utilized. The brine analyses were of greatest value in the interpretations concerning the northern and eastern portions of the map. In most instances, the chlorine content of the coal may be predicted satisfactorily from its location on the isochlor map.

When samples of both ground water and of coal were taken from the same mine, it was found that the chlorine in the coal was related more closely to the chlorine content of the associated ground water than to depth. The chlorine content of the coal is controlled by the composition of the ground water. In an approach toward equilibrium solutions intimately associated with the coal will take up or give off chloride ions as the ground water chlorine content increases or decreases. Whatever may have been the original chlorine content of the coal would have long since been obliterated, and the present chlorine content of coals within the Illinois Basin is the result of interaction with the currently associated ground water.

Based on the present study, it is felt that probably no coal in Illinois is sufficiently high in chlorine to render it unusable in high temperature boilers; however, special steps must be taken for utilization of some of the higher chlorine coals. The highest chlorine content of Illinois coals reported to date is about 0.65 percent, however, most are substantially lower. In Great Britain, coals with chlorine in excess of 1 percent have been utilized in power generating stations. Improved understanding of the factors operative in boiler fouling and corrosion will lead to additional measures to minimize this problem.

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